Journal of Chromatography, *630 (1993) 1-20*
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 711

Retention on non-polar adsorbents in liquid-solid chromatography

Effect of grafted alkyl chains

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(First received August 4th, 1992; revised manuscript received October 26th, 1992)

ABSTRACT

The retention of 39 molecular probes was measured on chemically bonded dense layers of (3,3-dimethylbutyl)dimethylsiloxy (DMB) and tetradecyldimethylsiloxy (C,,) substituents on silica as a function of the composition of the binary acetonitrile-water eluent. The sign of the "associated system peak" was also noted. The composition dependence of retention, measured as areal retention volume, could be described on both non-polar stationary phases by the two-parameter Snyder-Soczewinski equation and by the three parameter Schoenmakers equation in a broad but restricted composition range. The areal retention volume on the surface with grafted alkyl chains was equal to or higher than that on the non-swellable, smooth, non-polar DMB surface. Additional retention on the C_{14} surface increased with increasing adsorption force (retention) on the DMB surface and it was a function of the composition of the eluent. A possible interpretation of the sign of the "associated system peak" generated by the injection of a pure solute is also given in terms of solvation of the solute in the mobile phase and in terms of the modification of the non-polar adsorbent by the adsorbed solute.

INTRODUCTION

The problem of the effect of surface-bonded alkyl chains on retention will be addressed by comparing retention data measured on a tetradecyldimethylsiloxy (C_{14})-covered silica with those measured on a surface covered with a dense layer of (3,3-dimethylbutyl)dimethylsiloxy (DMB) substituents, depicted in Fig. 1. Several arguments speak in favour of the use of this special pair of adsorbents together with acetonitrile-water (AN-W) as a binary eluent for the study of this problem. First, with the corresponding dimethylaminosilanes as silylating agents, reproducible, dense layers of C_{14} and DMB can be grafted on widely differing silicon dioxide preparations [1]. Second, the excess adsorption isotherm from acetonitrile-water mixtures is nearly the same at the liquid–C_{14} and the liquid-DMB interface, as shown in Fig. 1 [2]. Third, the suitability of the DMB-covered surface as a smooth, non-swellable, non-polar standard has already been demonstrated by wetting experiments [3,4]. In fact, the DMB layer doubly shields the underlying matrix. The first dense layer formed by the methylenedimethylsiloxy base of the substituent implies a second dense layer formed by the *tert.*-butyl umbrella of the 3,3-dimethylbutyl group. Fourth, tetradecyldimethylsiloxy graft was preferred in this study to the widely used octadecyldimethylsiloxy (C_{18}) graft because latter shows a quasi-liquid-solid transition around 20°C. The corresponding transition of the C_{14} phase is around 0°C.

On the basis of these premises, differences in

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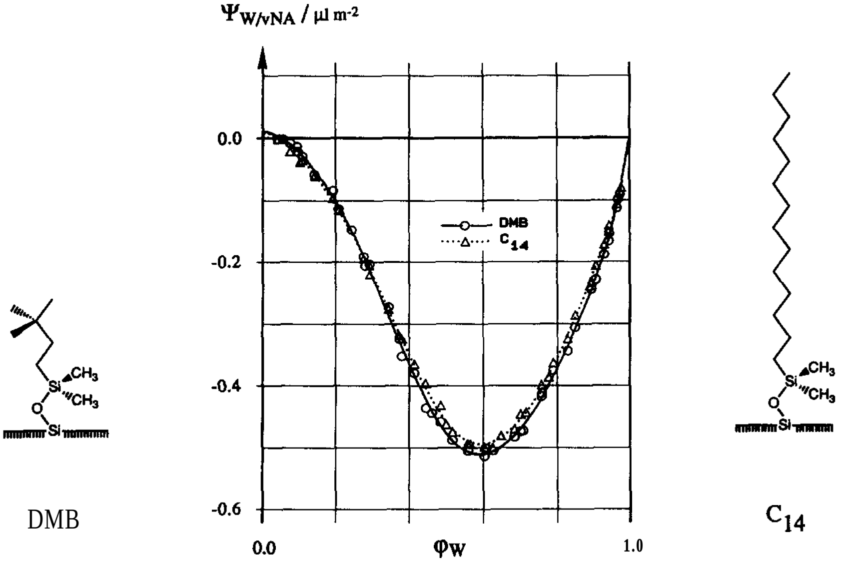

Fig. 1. Excess adsorption isotherms of water at the liquid-solid interface between acetonitrile-water as binary eluent and a dense layer of (0) (3,3-dimethylbutyl)dimethylsiloxy (DMB)- and (△) tetradecyldimethylsiloxy (C_{14})-covered silica as solid adsorbent as a function of the volume fraction of water, φ_W. Adsorption isotherms are given in terms of volume adsorbed per unit surface area with reference to the vNA Gibbs convention, i.e., nothing is adsorbed in terms of volume ($\Sigma\Psi_{i/vNA} = 0$).

retention on the C_{14} phase compared with those on the DMB standard at the same AN-W eluent composition can be clearly attributed to the presence of the C_{14} chains at the surface if retention is expressed using a column-independent intensive quantity. Consequently, following the proposal of Kiselev and Yashin [5], retention data will be given as areal retention volumes, V_S (μl/m$^2 \equiv$ nm), derived from a net retention volume which is in accordance with Gibbs' description of excess adsorption at the liquid-solid interface [6,7]. Arguments in favour of the areal retention volume and the unsuitability of the widely applied capacity factor, *k'*, are expressed hereafter (see below).

Successful application of adsorbents with grafted n-alkyl chains in liquid-solid chromatography has largely stimulated the study of their adsorption properties. Primitively, they have been considered as solids covered with a chemically immobilized liquid monolayer at their surface. Early investigations have demonstrated that retention increases with increasing "carbon loading", *i.e.*, on grafts with longer chain length and/or increasing density (ligand surface concentration) of the surface layer [8–21]. Unger and co-workers [22,23] were the first to point out that retention must also depend on the available surface area of the stationary phase in the column, *S*, and proposed to examine the dependence of log(retention/S) as a function of the chain length of the graft. It has been shown that this normalized logarithmic retention is a linear function of the chain length and/or the carbon content per unit surface area. The drawback of these and subsequent studies had been the use of ill-defined or incompletely surface-substituted adsorbents. Scott and Kucera [11] demonstrated the lack of correlation between retention and surface coverage or chain length for commercial adsorbents. In several studies, laboratory-made silica-based alkyldimethylsiloxy-covered adsorbents have been applied, but surface treatment was made with inefficient silylating agents such as chloro- or methoxyalkyldimethylsilanes. With such agents, the ligand surface concentration decreases with increasing chain length of the alkyl substituent. It has been shown that retention increases with increasing chain length of the graft up to about ten carbons, then retention levels off for longer alkyl chain grafts [24]. This type of dependence may be due to the combined effect of increasing chain length and, parallel to that, a decreasing surface coverage.

Lork [25] confirmed this dependence on a series of stationary phases with constant but very low (Γ_{sox} = 2.1 μmol/m^2) areal concentration of the alkyldimethylsiloxy graft. In fact, the surface concentration amounted to about 60% of that obtained with alkyldimethyl(dimethylamino)silane as silylating agent [1]. This general picture is even more confusing considering the observation of several workers that the nature of the function describing the dependence of retention on chain length or on areal concentration of the graft is different for different types of solutes [26,27].

In summary, despite numerous efforts to measure and understand the influence of the chain length and areal concentration of the grafted chains, interpretation of the results of these studies is difficult. Experiments have always been conducted either on incompletely silylated surfaces or on surfaces where the areal concentration of the alkyl graft depended on the chain length. Even on surfaces with the densest layers, silanol groups contribute to adsorption. In Fig. 1 the slight positive water adsorption at low water concentrations has been shown to be due to specific adsorption of water on silanols "visible" across the graft by the small water molecule [2]. Therefore, incompletely silylated silica is certainly a heterogeneous adsorbent, hence it is not surprising that the areal concentration of the graft influences retention. Also, it is unfortunate that retention has generally been reported in terms of the capacity factor, *k'*, which is essentially the relative retention of the solute referred to that of a solute believed to be unretained. Considering the multitude of "unretained" solutes proposed and applied in these studies, one has to conclude that the capacity factor only allows comparison of retention data obtained in one study by a given worker on a given column at a given eluent composition. It is important to note that capacity factor is not an intensive quantity even if the zero retention is determined relative to a hold-up volume defined by a given Gibbs convention.

The aim of this paper is to report retention data of a series of solutes of differing polarity on two silica-based adsorbents covered with a dense, chemically bonded, non-polar monolayer, one with and the other without grafted C_{14} alkyl chains. Retention will be given as areal retention volume referred to the BET surface area of the stationary phase in the column.

THEORETICAL BACKGROUND

The relationship between adsorption and retention in liquid-solid chromatography with binary eluents has been treated extensively [6,7,28]. In this section will be summarized the underlying principles and the necessary equations for the evaluation and interpretation of the experimental data.

The Gibbs convention

Mixtures of non-electrolytes are nearly ideal concerning the additivity of the volume of the components, *i.e.*, the partial volumes can be equated to those of the pure components with sufficient precision. Therefore, the mass balance of a component, *i*, in the column at equilibrium with a multicomponent mixture can be replaced by the volume balance

$$V_{\kappa,i} = \varphi_i V_{\mu/\mathrm{CX}} + S\Psi_{i/\mathrm{CX}} \tag{1}$$

where $V_{\kappa,i}$ is the total material content of component, *i*, in terms of volume at adsorption equilibrium under isocratic conditions (the isocratic capacity, κ, of *i*), φ_i is the volume fraction of *i* in the bulk liquid (eluent), $V_{\mu/\mathrm{CX}}$ is the volume of the eluent in the column (μ: mobile phase), S is the surface area of the adsorbent and $\Psi_{i/\mathrm{CX}}$ is the adsorbed volume of component *i* per unit surface area. The bulk liquid volume and the adsorbed volume are defined quantities only if a "convention" is agreed upon (CX: Convention X). For a system consisting of a binary eluent of components A and B and a solute (su), eqn. 1 represents three independent relationships with four unknowns, $V_{\mu/\mathrm{CX}}, \Psi_{\mathrm{A/CX}}, \Psi_{\mathrm{B/CX}}$ and $\Psi_{\mathrm{su/CX}}$. Following Gibbs' proposal, a convention has to be stated in order to obtain the fourth equation. For several reasons the convention expressed in eqn. 2 is particularily attractive:

$$\Sigma \Psi_{i/\mathrm{vNA}} = 0 \tag{2}$$

i.e., the sum of the adsorbed amount in terms of volume is zero. This convention is named the **vNA-convention**; Nothing is Adsorbed in terms of volume. Obviously, with this convention the total liquid in the column is considered as the mobile phase and eqn. 3 holds:

$$V_{\kappa/\mathrm{tot}} = V_{\mu/\mathrm{vNA}} \tag{3}$$

where $V_{\mu/\mathrm{vNA}}$ is the hold-up volume. This hold-up volume is independent of the eluent composition if the partial molar volumes of all components in the mixture as well as in the adsorbed state are equal to the molar volume of the pure components.

Retention

With a binary eluent, A/B, the retention volume, $V_{R,i}$, of a component, i (= su, A, B), is given by [2,6]

$$V_{R,i}=\left(\frac{\partial V_{\kappa,i}}{\partial\varphi_i}\right)_{\varphi_A^0}-\varphi_i^0\left(\frac{\partial V_{\kappa,\mathrm{tot}}}{\partial\varphi_i}\right)_{\varphi_A^0} \tag{4}$$

where the superscript zero refers to concentrations at equilibrium in the column before injection. Combination of eqns. 1, 3 and 4 gives the retention volume of a solute, su:

$$V_{R,su}=V_{\mu/vNA}+S\left(\frac{\partial\Psi_{su/vNA}}{\partial\varphi_{su}}\right)_{\varphi_A^0};\qquad \varphi_{su}\to 0 \tag{5}$$

and the retention volume of the injection of component A or B of the binary eluent:

$$V_{R,A}=V_{R,B}=V_{\mu/vNA}+S\left(\frac{\partial\Psi_{A/vNA}}{\partial\varphi_A}\right)_{\varphi_A^0} \tag{6}$$

called the system peak (SP) or concentration peak. Application of eqn. 4 to labelled components of the eluent, A* and B*, and combination of the results give the necessary relationship for the experimental determination of the hold-up volume:

$$V_{\mu/vNA}=\varphi_A V_{R,A^*}+\varphi_B V_{R,B^*} \tag{7}$$

The hold-up volume, $V_{\mu/vNA}$, has been shown to be independent of eluent composition [2,29]. Its knowledge allows the calculation of the net retention volume:

$$V_{N,su/vNA}=V_{R,su}-V_{\mu/vNA} \tag{8}$$

The areal retention volume is defined as

$$V_{S,su/vNA}=\frac{1}{S}\cdot V_{N,su/vNA}=\left(\frac{\partial\Psi_{su/vNA}}{\partial\varphi_{su}}\right)_{\varphi_A^0} \tag{9}$$

The areal retention volume, $V_{S,su/vNA}$, can be identified as the slope of the areal excess isotherm of the solute at the eluent composition. It is an intensive, model-independent characteristic of solute retention. It is related to the solute adsorption equilibrium at the eluent composition, φ_A^0, and as such it can be a positive or a negative quantity. This representation of solute retention does not suppose the existence of any autonomous liquid stationary phase, and implies that solute retention in liquid–solid chromatography is an interfacial phenomenon necessarily proportional to the extent of the adsorbent surface area in thecolumn, S. Obviously, the determination of S requires the use of a non-chromatographic technique. Nevertheless, using this representation, areal retention volumes are independent of column construction and adsorbent morphology. Hence they allow comparison of retention data between different laboratories.

Capacity factor

The widely used capacity factor of a solute, k'_{su}, is the ratio of a reduced retention volume, $V_{N,su}$, and the retention of a substance believed to traverse the column with the same velocity as that of the mobile phase, V_0:

$$k'_{su}=\frac{V_{R,su}-V_0}{V_0}=\frac{V_{N,su}}{V_0} \tag{10}$$

Obviously, the capacity factor is not suitable to report system-independent retention data, for several reasons. When using eqn. 10, it is believed that V_0 is a correct hold-up volume equal to the volume of a mobile bulk liquid in the column. However, in a liquid-solid adsorption system there is no possibility of identifying a liquid of bulk composition and a distinct layer at the interface having a different composition. Therefore, the proposal to determine the hold-up volume by injection of a “non-adsorbed” component leads to a wide variety of hold-up volume definitions. Hold-up volume differences of up to 100% can be found following different methods proposed for its determination [6,7,11,23, 30–35]. Moreover, this hold-up volume also includes column tubing contributions making it dependent on the actual measuring system. Even if everyone agreed to report capacity factors using a hold-up volume belonging only to the column and referring to a given Gibbs convention (e.g., $V_0=V_{\mu/vNA}$), the resulting $k'_{su/vNA}$ would still not be an intensive property of the solute. In fact, the net retention volume, $V_{N,su/NA}$, is proportional to the surface area of the adsorbent but the hold-up volume, $V_{\mu/vNA}$, is not. As an example, in two columns of similar volume packed with two adsorbents having surface areas of S and 2S, the net retention will differ by a factor of 2 whereas the hold-up volume may be about the same. For reasons outlined above, it is proposed that liquid chromatographic data be reported in terms of areal retention volumes instead of the capacity factor.

The capacity factor or "mass distribution coefficient" is defined as the ratio of the amounts of solute in the stationary phase and in the mobile phase. Based on this definition, the capacity factor related to the vNA convention, $k'_{su/vNA}$, can be interpreted as follows. The relationship of eqn. 9 between the adsorption isotherm of the solute, $\Psi_{su/vNA}$, at the eluent composition φ^0_A and its concentration in the eluent can be written as

$$V_{N,su/vNA}/S = \Psi_{su/vNA}/\varphi_{su}; \quad \varphi_{su} \rightarrow 0 \tag{11}$$

In fact, the value of the derivative of the solute isotherm, $\Psi_{su/vNA}(\varphi_{su})$, with respect to the volume fraction of the solute is equal to the ratio given in eqn. 11 at $\varphi_{su} \rightarrow 0$. Use of the experimental definition of the capacity factor given in eqn. 10 with $V_0 = V_{\mu/vNA}$ and eqns. 1, 8 and 11 gives

$$k'_{su/vNA} = \frac{V_{N,su/vNA}}{V_{\mu/vNA}} = \frac{S\Psi_{su/vNA}}{\varphi_{su} V_{\mu/vNA}} = \frac{S\Psi_{su/vNA}}{V_{K,su} - S\Psi_{su/vNA}} \tag{12}$$

Eqn. 12 shows that this capacity factor is the ratio of the excess adsorbed amount of the solute (expressed as volume) and of the non-adsorbed part contained in the total liquid volume [36]. The excess adsorbed amount of the solute, and hence also the capacity factor related to the vNA convention, $k'_{su/vNA}$, can be positive or negative.

Areal retention volume, capacity factor and distribution coefficient

The relationship between the capacity factor and the areal retention volume referring to the vNA convention is obtained from eqns. 9 and 10 to give

$$S V_{S,su/vNA} = k'_{su/vNA} V_{\mu/vNA} \tag{13}$$

the link being given by the adsorbent surface area and the hold-up volume. With the necessary changes, eqn. 13 is of general validity for any hold-up definition.

Unlike the capacity factor, the distribution coefficient of the solute, $K_{D,su}$, defined as the ratio of the solute concentration near the interface and that in the bulk liquid, would be a correct intensive quantity to characterize solute retention. However, with convention vNA it is meaningless. In fact, Gibbs' interpretation of adsorption by defining excess quantities is not a model, it does not locate anywhere the adsorbed excess of the solute and it does not define any liquid stationary phase. Application of the vNA (or any other) Gibbs convention does not allow the calculation of a distribution coefficient, $K_{D,su/vNA}$, because only knowledge of an adsorption excess isotherm does not permit the calculation of a local concentration near the interface.

In order to compare our data with literature values, a retention volume is needed that permits the calculation of a distribution coefficient. This can be found by introducing an unusual Gibbs convention as follows. As has been shown, if the partial molar volumes of eluent components in both the bulk liquid and the adsorbed state are the same as their molar volume in the pure state, the hold-up volume, $V_{\mu/vNA}$, is equal to the volume of the total liquid phase in the column. Let us now define a film of thickness τ parallel to the surface of the adsorbent as stationary phase, designated by ϑ, and attribute all adsorption to this film of uniform composition. Applying this τ convention, derived from the vNA convention, the volume of the stationary liquid, $V_{\vartheta/\tau}$, is equal to τS. The remaining volume of the total liquid is now considered as the mobile phase, and consequently the hold-up volume is given by

$$V_{\mu/\tau} = V_{\mu/vNA} - \tau S \tag{14}$$

i.e., it is defined with reference to the hold-up volume, $V_{\mu/vNA}$. The necessary relationships for the calculation of the corresponding areal retention volume, $V_{S,su/\tau}$, the related capacity factor, $k'_{su/\tau}$, and the distribution coefficient, $K_{D,su/\tau}$, are as follows:

$$V_{S,su/\tau} = V_{S,su/vNA} + \tau \tag{15}$$

$$k'_{su/\tau} = \frac{V_{S,su/vNA} + \tau}{(V_{\mu/vNA}/S) - \tau} \tag{16}$$

$$K_{D,su/\tau} = k'_{su/\tau} V_{\mu/\tau}/V_{\vartheta/\tau} = 1 + V_{S,su/vNA}/\tau \tag{17}$$

On the areal retention volume scale, transformation of the vNA convention to the τ convention represents a simple shift by the arbitrarily chosen layer thickness, τ. On the capacity factor scale, however, not only the zero point but also the units change owing to such a transformation, as illus-

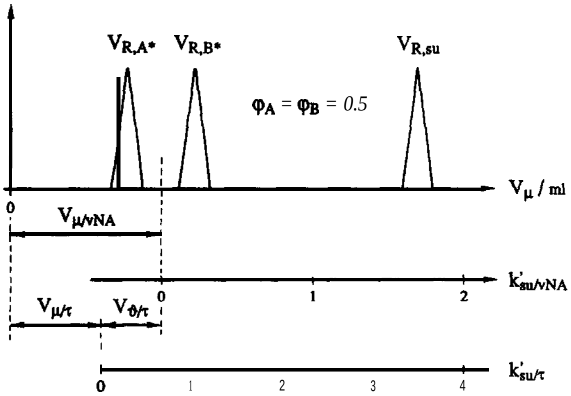

Fig. 2. Illustration of eqns. 14-17 on a hypothetical example where $\varphi_A = \varphi_B = 0.5$. In this case the hold-up volume, $V_{\mu/vNA}$, is exactly mid-way between the retention volumes of the labelled components of the binary eluent, V_{R,A^*} and V_{R,B^*}. The scale of the capacity factor, $k'_{su/vNA}$, is related to this hold-up volume. The volume of the hypothetical stationary phase, $V_{\vartheta/\tau} = \tau S$, is deduced from the total mobile phase volume, $V_{\mu/vNA}$, to give a new hypothetical mobile phase volume, $V_{\mu/\tau}$, which is the unit of the second capacity factor scale, $k'_{su/\tau}$.

trated in Fig. 2. For a solute having zero excess adsorption, $V_{S,su/vNA}$ is equal to zero. Such a solute has a uniform concentration in the whole liquid phase ("mobile, μ" and "stationary, ϑ") and eqn. 16 gives $k'_{su/\tau} = V_{\vartheta/\tau}/V_{\mu/\tau}$, the phase ratio, and eqn. 17 gives $K_{D,su/\tau} = 1$.

Choice of the stationary layer thickness, τ

For the columns applied in this study a column hold-up volume corrected for the extra-column volumes of tubings and connections was measured and reported in ref. 2 to give $V_{\mu/vNA}$ = 2.1-2.3 ml. The surface area of the adsorbent in the column was around S = 340 m^2, giving a liquid volume per unit surface area of $V_{\mu/vNA}/S \approx 6.5$ $\mu l/m^2 \equiv$ 65 A. Obviously, to avoid negative mobile phase volumes, the value of the thickness, τ, must be less than 65 Å. On the other hand, there is also a lower limit of the layer thickness to ensure that surface concentrations are always positive and monotonously increasing functions of bulk concentrations, which is a thermodynamic necessity [7]. This minimum thickness is about 15 Å in AN-W mixtures on both surfaces (C_{14} and DMB) as shown by the corresponding excess adsorption isotherms [2]. In conclusion, a value of 15 Å is proposed for τ. With this layer thickness, the volume of the stationary phase in our columns is $V_{\vartheta/\tau}/S$ = 1.5 $\mu l/m^2$ and that of the mobile phase $V_{\mu/\tau}/S \approx 6.5 - 1.5 = 5.0$ $\mu l/m^2$, both referred to unit surface area, to give a phase ratio of $V_{\vartheta/\tau}/V_{\mu/\tau} \approx 0.30$. As an example, for a solute retained with $V_{S,su/vNA}$ = 2.0 $\mu l/m^2$, the fraction in the τ interfacial layer is 41% of the total.

Obviously, the choice of the thickness τ = 15 Å is only valid for the actual working system, *i.e.*, AN-W binary eluent mixtures on DMB and C_{14} surfaces. In other systems the choice of a different thickness may be necessary.

Concluding remarks

It should be emphasized that the introduction of the τ convention was simply a device to enable literature proposals to be applied for the description of the composition dependence of retention. In fact, these proposals are based on models assuming the existence of a stationary phase of given volume. Such a model implies that negative net retention volumes do not exist and leads to equations relating the logarithm of net retention to the eluent composition. It was therefore necessary to transform the areal retention volumes related to the vNA convention (which permits negative values) to areal retention volumes referred to an appropriate τ convention which excludes negative values, Actually, the minimum of such a layer thickness identified as the minimum slope of the binary excess isotherm, and this choice implies that areal retention volumes of any solute calculated with the corresponding hold-up volume are never negative. This statement remains valid as long as the binary adsorption equilibrium is not considerably altered by the solute, which is always supposed to be present in infinite dilution. All solutes used in this study fulfilled this requirement, and consequently eqn. 17 for the calculation of a distribution coefficient will always be applicable.

EXPERIMENTAL

Materials

The precipitated silica for the preparation of the stationary phases was LiChrosorb Si 100 from Merck (Darmstadt, Germany) with a nominal particle diameter of 10 μm and a pore diameter of 100 A. Nitrogen adsorption isotherms were measured at

77 K. BET evaluation of the isotherm in the relative pressure range $0.05 < P_e/P_0 < 0.23$ gave a specific surface area of $s = 298 \pm 3$ m^2/g (average of three determinations). Nitrogen for adsorption experiments (99.999%) and liquid nitrogen for thermostating (99.8%) were obtained from Carbagas (Lausanne, Switzerland). The silylating agents (purity > 98%) N-[(3,3-dimethylbutyl)dimethylsilyl]-N,N-dimethylamine and N-(tetradecyldimethylsilyl)-N, N-dimethylamine were synthesized in our laboratory [37]. Acetonitrile (AN) for HPLC from Ammann Technik (Kölliken, Switzerland) was used as received. Doubly distilled water (W) was prepared by distilling deionized water over potassium permanganate in a Fontavapor-285 Pyrex glass still from Büchi (Flawil, Switzerland). The solutes, research-grade deuterated compounds (isotope purity >99.5%) D^2H_2O and CD^2H_3CN (W* and AN*) from Chemie Uetikon (Uetikon, Switzerland) and research-grade 1-alkanols, 2-alkanols, 2-alkanones, 1-alkyl acetates, n-alkanes and 2,2-dimethylalkanes from Fluka (Buchs, Switzerland), were used as received.

Chromatographic columns

Column materials were prepared by reaction of vacuum-dried (10^{-3} Torr at 120°C for 10 h) LiChrosorb Si 100 with R-dimethyl(dimethylamino)silane (*ca.* 15 μmol/m^2) at 180°C for 100 h, following the reported procedure [1]. Surface concentrations of the siloxy substituents, Γ_{sox}, listed in Table I were calculated with the carbon content of the silylated products measured by elemental analysis and with the BET specific surface area of the unreacted silica, using the equation given previously [38]. The columns used and the procedure for column packing were described in detail previously [39]. Columns were dried at 120°C in a stream of argon and the mass of the stationary phase in the column, m_ϑ, was determined by weighing (see Table I). This operation was repeated after having finished all chromatographic experiments. After 2 years of use no significant loss of the stationary phase mass was observed [39]. The surface area of the adsorbent in the columns was assumed to be equal to that of the unmodified silica [40], given by

$$S = sm_\vartheta\{1 + 10^{-6}\Gamma_{\mathrm{sox}}s[M(\mathrm{R}) - \mathrm{corr}]\}^{-1} \qquad (18)$$

where s (m^2/g) is the specific surface area of the unmodified silica, Γ_{sox} (μmol/m^2) is the surface concentration of the graft, M(R) is the molar mass of the trialkylsilyl substituent and corr (= 2.5) is a correction for proton substituted and water desorbed during silylation [38]. Column characteristics are listed in Table I.

TABLE I

CHARACTERISTICS OF THE STATIONARY PHASES AND COLUMNS USED

Γ_{sox} is the surface concentration of the akyldimethylsiloxy substituent, m_ϑ is the mass of the adsorbent and S is the surface area of the adsorbent, assumed to be equal to the surface area of the silicon dioxide in the column. Standard deviations are given in the bottom row.

Stationary phase		Column	
Graft	Γ_{sox} (μmol/m^2)	m_ϑ (g)	S (m^2)
DMB	3.85	1.302	334
C14	4.09	1.547	352
S.D.	±0.02	~0.002	±4

Apparatus

Nitrogen adsorption isotherms were measured with a modified Sorptomatic 1800 apparatus from Carlo Erba (Milan, Italy) [38]. The carbon contents of the column materials were determined with a Model 240B elemental analyser (Perkin-Elmer, Norwalk, CT, USA).

The chromatographic apparatus was described in detail previously [41]. It was an assembly of a Model 510 solvent-delivery pump, a Model U6K injector (loop volume 1 ml) and a Model 410 differential refractometer detector (cell volume 10 μl), all from Waters (Milford, MA, USA). Columns were mounted in parallel in a thermostated bath at 20.0 ± 0.1°C. Retention times (t_{R}) were measured with a Model SP4290 integrator (Spectra-Physics, Santa Clara, CA, USA). The flow-rate of the eluent, $\dot{V}_\mu$, was measured at 20.0 ± 0.1°C with a reproducibility of 0.005 ml/min; it had a long-term stability of ±0.2%. The nominal flow-rate was 2.0 ml/min throughout. Retention volumes (V_{R}) were calculated from retention times and the actual flow-rate. The mean column pressure *(P,)* was approximately half of the inlet pressure (typical values P_c = 20-50 bar).

Experiments

General. The binary AN-W eluent mixture of the appropriate composition, prepared by weighing an amount sufficient for all experiments on both columns, was degassed by bubbling helium through the mixture and kept under a slight helium overpressure (0.07 bar) during the experiments. The columns were equilibrated with the eluent of a given composition for 10 min.

Hold-up volume. First, pure W and AN were injected in order to identify the binary concentration peak (system peak), followed by mixtures of AN–W* and AN*-W of the same composition (mol/mol) as that of the eluent to give the retention volumes $V_{\mathrm{R,W^*}}$ and $V_{\mathrm{R,AN^*}}$ (W* and AN* represent deuterated water and acetonitrile, respectively). The system hold-up volume, $V_{\mu/\mathrm{NA}}$, was calculated with eqn. 7.

Solutes. Members of different homologous series (1-alkanols, 2-alkanols, 2-alkanones, 1-alkyl acetates, n-alkanes and 2,2-dimethylalkanes) were injected and their retention times were measured. Weakly retained solutes were dissolved in the binary eluent in a ratio of up to 1:20 (v/v); solid solutes were injected in ethanol solution. Typical volumes injected were 0.5-1.5 μl, always aiming at the smallest possible reproducible signal. Measurements were made on both surfaces at eluent compositions listed in Table II and repeated at least seven times at each eluent composition. The reproducibility of the retention volume of the deuterated eluent components was $\sigma_{\mathrm{rel}} = \pm 0.4\%$ and that of the solutes was $\sigma_{\mathrm{rel}} \leqslant \pm 0.8\%$. Each solute, except solids, was also injected as a pure substance for the determination of the sign of the associated system peak.

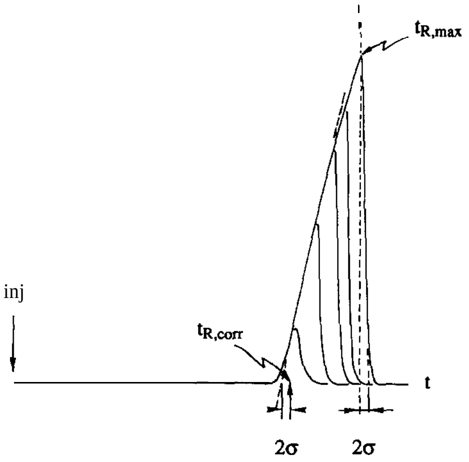

Fig. 3. Evaluation of the retention time of a solute eluting with asymmetric peaks. It shows the superposition of a series of fronting peaks obtained by injecting different volumes of *n*-heptane (2.0–0.1 μl) at φ_{W} = 0.293 onto the DMB-covered surface. It was assumed that the contribution to the standard deviation of the peak dispersion on the fronting side can be estimated from the dispersion of the (non-tailing) rear side of the peak. With this hypothesis, the retention time of an infinitesimal sample, $t_{\mathrm{R,corr}}$, could be constructed.

Evaluation of asymmetric peaks

In Fig. 3 are shown chromatograms of n-heptane on the DMB surface at the eluent composition φ_{W} = 0.293. It was observed that the chromatograms obtained with different amounts injected followed the same trace at the fronting side. In order to determine the retention time at zero sample volume, it was assumed that the peak broadening in the column could be estimated from the narrow rear side of the peak. If this side corresponded to half of a Gaussian distribution, the standard deviation of the peak broadening can be determined from the distance between the mode and the intercept of the tangent of the rear side of the peak with the baseline, equalling 2σ (see Fig. 3). Admitting that the same peak broadening is valid for the front side, the correct peak position should be at a distance of 2σ from the intercept of the tangent of the front side with the baseline. This evaluation was applied to all n-alkanes and 2,2-dimethylalkanes.

In several instances the opposite situation was found, with tailing peaks. Injection of different amounts of 1-butyl acetate onto the C_{14} surface at the eluent composition φ_{W} = 0.602 gave the mirror image of Fig. 3. For the determination of the peak position at zero amount injected, the analogous evaluation was applied. Tailing peaks were observed on both columns for 1-alkanols and 2-alkanols at $V_{\mathrm{S,su/vNA}} >$ 12-15 μl/m^2, for 2-alkanones at $V_{\mathrm{S,su/vNA}} >$ 3-4 μl/m^2 and for 1-alkyl acetates at $V_{\mathrm{S,su/vNA}} >$ 7-8 μl/m^2.

Retention data

In Table II are listed the experimental areal retention volumes of solutes at different eluent compositions, φ_{W}, referring to the vNA convention on the DMB-covered surface, $V^{\mathrm{DMB}}_{\mathrm{S,su/vNA}}$, and on the C_{14}-covered surface, $V^{\mathrm{C_{14}}}_{\mathrm{S,su/vNA}}$, calculated with eqn. 9.

TABLE II

AREAL RETENTION VOLUMES, $V_{\mathrm{S,su/v}NA}$(µl/m^2), ON DMB- AND C$_{14}$-COVERED STATIONARY PHASES AT DIFFERENT VOLUME FRACTIONS OF WATER, φ_W, IN THE ACETONITRILE-WATER BINARY ELUENT

The column temperature was 20.0 ± 0.1°C. Data on the C$_{14}$-covered adsorbent are in the second rows *in italics*. The sign of the associated system peak ($^+$ if it is rich in AN) given as superscript.

Solute	φ_W														
	0.028	0.057	0.095	0.193	0.293	0.373	0.445	0.518	0.602	0.685	0.757	0.829	0.908	0.946	0.973
1-Alkanols															
Methanol	0.34$^-$	0.14$^-$	0.05$^-$	-0.36$^+$	-0.43$^+$	-0.46$^+$	-0.50$^+$	-0.39$^+$	-0.48$^-$	-0.20$^-$	-0.19'	0.14$^-$	0.44$^-$	0.79$^-$	1.24-
	0.20-	0.05	*-0.05$^-$*	*-0.33$^+$*	*-0.45$^+$*	*-0.46$^+$*	*-0.51$^+$*	*-0.47$^+$*	*-0.40$^-$*	*-0.18$^-$*	*-0.17$^-$*	0.09	*0.32$^-$*	*0.70$^-$*	*1.08$^-$*
Ethanol	0.16'	0.10$^+$	0.09$^+$	-0.18$^+$	-0.26$^+$	-0.24$^+$	-0.22$^+$	-0.13$^+$	0.12$^+$	0.19$^+$	0.34'	0.76$^-$	1.32$^-$	2.53'	3.66$^-$
	0.25$^-$	*0.08$^+$*	*0.03$^+$*	*-0.17$^+$*	*-0.23$^+$*	*-0.25$^+$*	*-0.20$^+$*	*-0.15$^+$*	*0.20$^+$*	*0.18$^+$*	*0.30$^-$*	*0.68$^-$*	*1.21$^-$*	*2.65$^-$*	*3.80$^-$*
1-Propanol	0.22$^+$	0.17$^+$	0.16$^+$	0.00+	0.10$^+$	0.23$^+$	0.57$^+$	0.58$^+$	0.99$^+$	1.39$^+$	2.04$^+$	3.04$^+$	6.03$^+$	9.25$^+$	12.1$^+$
	0.42$^+$	*0.24$^+$*	*0.20$^+$*	*0.06$^+$*	*0.17$^+$*	*0.29$^+$*	*0.55$^+$*	*0.61$^+$*	*1.13$^+$*	*1.36$^+$*	*1.96$^+$*	*2.58$^+$*	*6.05$^+$*	*9.72$^+$*	*14.8$^+$*
1-Butanol	0.34$^+$	0.31$^+$	0.31$^+$	0.30$^+$	0.51$^+$	0.90$^+$	1.41$^+$	2.10$^+$	2.93$^+$	4.28$^+$	6.38$^+$	10.0$^+$	19.4$^+$	28.9$^+$	40.4$^+$
	0.58$^+$	*0.45$^+$*	*0.38$^+$*	*0.39$^+$*	*0.56$^+$*	*1.01$^+$*	*1.52$^+$*	*2.08$^+$*	*3.13$^+$*	*4.52$^+$*	*6.59$^+$*	*10.0$^+$*	*22.0$^+$*	*35.7$^+$*	*57.3$^+$*
1-Pentanol	0.51$^+$	0.48$^+$	0.49$^+$	0.59$^+$	1.04$^+$	1.74$^+$	2.67$^+$	3.73$^+$	5.88$^+$	9.28$^+$	16.1$^+$	26.7$^+$	60.8$^+$	94.3$^+$	143$^+$
	0.86$^+$	*0.74$^+$*	*0.70$^+$*	*0.95$^+$*	*1.29$^+$*	*2.10$^+$*	*3.01$^+$*	*4.18$^+$*	*6.77$^+$*	*10.7$^+$*	*17.7$^+$*	*31.6$^+$*	*80.9$^+$*	*143$^+$*	*231$^+$*
1-Hexanol	0.63$^+$	0.67$^+$	0.75$^+$	1.01$^+$	1.76$^+$	2.84$^+$	4.33$^+$	6.47$^+$	11.2$^+$	18.3$^+$	36.7$^+$	73.1$^+$	-	-	-
	1.20$^+$	*1.16$^+$*	*1.19$^+$*	*1.62$^+$*	*2.41$^+$*	*3.68$^+$*	*5.32$^+$*	*7.71$^+$*	*13.9$^+$*	*23.4$^+$*	*48.6$^+$*	*101$^+$*	-	-	-
1-Heptanol	0.87$^+$	0.91$^+$	1.02$^+$	1.54$^+$	2.52$^+$	3.96$^+$	6.14$^+$	10.4$^+$	17.0$^+$	36.4$^+$	-	-	-	-	-
	1.53$^+$	*1.54$^+$*	*1.84$^+$*	*2.35$^+$*	3.53'	*5.19$^+$*	*7.61$^+$*	*14.3$^+$*	*21.6$^+$*	*54.3$^+$*	-	-	-	-	-
1-Nonanol	1.40$^+$	1.58$^+$	1.79$^+$	3.26$^+$	5.48$^+$	9.50$^+$	14.8$^+$	23.2$^+$	-	-				-	-
	3.14$^+$	*3.54$^+$*	*4.03$^+$*	*6.26$^+$*	*10.4$^+$*	*15.8$^+$*	*27.6$^+$*	*44.5$^+$*	-	-				-	-
1-Undecanol	2.11$^+$	2.61$^+$	2.98$^+$	6.11$^+$	10.4$^+$	17.0$^+$	36.6$^+$	54.2$^+$	-	-	-	-	-	-	-
	5.81$^+$	*6.92$^+$*	*8.43$^+$*	*15.1$^+$*	*26.1$^+$*	*42.9$^+$*	-	-	-	-	-	-	-	-	-
1-Tridecanol	282	3.81	4.39	9.37	17.5	30.9	-	-	-	-	-	-	-	-	-
	10.4	133	17.1	32.0	61.1	108	-	-	-	-	-	-	-	-	-
1-Tetradecanol	3.36	4.59	5.74	-	-	-	-	-	-	-	-	-	-	-	-
	13.9	*18.2*	*24.0*	-	-	-	-	-	-	-	-	-	-	-	-
1-Hexadecanol	*4.78*	*7.02*	*10.4*	-	-	-	-	-	-	-	-	-	-	-	-
	23.1	*33.7*	*44.0*	-	-	-	-	-	-	-	-	-	-	-	-
1-Octadecanol	*6.79*	*9.59*	-	-	-	-	-	-	-	-	-	-	-	-	-
	38.1	*57.0*	-	-	-	-	-	-	-	-	-	-	-	-	-
1-Eicosanol	*9.57*	*14.1*	-	-	-	-	-	-	-	-	-	-	-	-	-
	613	*99.4*	-	-	-	-	-	-	-	-				-	-
2-Alkanols															
2-Propanol	0.28$^+$	0.18$^+$	0.17$^+$	0.00+	-0.02$^+$	0.05$^+$	0.14$^+$	0.31$^+$	0.56$^+$	1.04$^+$	1.37$^+$	2.28$^+$	4.62$^+$	7.17$^+$	10.0$^+$
	0.42$^+$	*0.18$^+$*	*0.17$^+$*	*0.06$^+$*	*0.00$^+$*	*0.06$^+$*	*0.15$^+$*	*0.31$^+$*	*0.71$^+$*	*0.90$^+$*	*1.32$^+$*	*2.04$^+$*	*4.49$^+$*	*7.72$^+$*	*11.5$^+$*
2-Butanol	0.34$^+$	0.31$^+$	0.23$^+$	0.24$^+$	0.40$^+$	0.73$^+$	1.09$^+$	1.64$^+$	2.14$^+$	3.20$^+$	4.48$^+$	7.20$^+$	14.3$^+$	20.9$^+$	30.6$^+$
	0.58$^+$	*0.40$^+$*	*0.37$^+$*	*0.34$^+$*	*0.45$^+$*	*0.77$^+$*	*1.12$^+$*	*1.68$^+$*	*2.39$^+$*	*3.20$^+$*	*4.52$^+$*	*6.93$^+$*	*15.2$^+$*	*24.6$^+$*	*40.5$^+$*
2-Pentanol	0.51$^+$	0.49$^+$	0.44$^+$	0.59$^+$	0.93$^+$	1.50$^+$	2.25$^+$	3.12$^+$	4.72$^+$	7.05$^+$	11.3$^+$	19.9$^+$	43.4$^+$	67.7$^+$	109$^+$
	0.86$^+$	*0.64$^+$*	*0.67$^+$*	*0.79$^+$*	*1.12$^+$*	*1.75$^+$*	*2.46$^+$*	*3.48$^+$*	*5.20$^+$*	*7.53$^+$*	*11.9$^+$*	*21.2$^+$*	*53.1$^+$*	*92.0$^+$*	*161$^+$*
2-Hexanol	0.63$^+$	0.67$^+$	0.66$^+$	1.01$^+$	1.64$^+$	2.56$^+$	3.84$^+$	5.47$^+$	9.05$^+$	15.0$^+$	27.5$^+$	53.7$^+$	-	-	-
	1.14$^+$	*1.05$^+$*	*1.09$^+$*	*1.45$^+$*	*2.07$^+$*	*3.22$^+$*	*4.94$^+$*	*6.15$^+$*	*11.1$^+$*	*17.6$^+$*	*32.0$^+$*	*64.9$^+$*	-	-	-

(Continued on p.10)

TABLE II *(continued)*

Solute	φ_{W}														
	0.028	0.057	0.095	0.193	0.293	0.373	0.445	0.518	0.602	0.685	0.757	0.829	0.908	0.946	0.973
2-Alkanones															
Propanone	0.16^{+}	0.18^{+}	0.26^{+}	0.12^{+}	0.28^{+}	0.44^{+}	0.70^{+}	0.89^{+}	1.08^{+}	1.57^{+}	1.81^{+}	2.51^{+}	3.91^{+}	5.84^{+}	8.69^{+}
	0.31^{+}	*0.18*$^{+}$	*0.20*$^{+}$	*0.17*$^{+}$	*0.28*$^{+}$	*0.53*$^{+}$	*0.60*$^{+}$	*0.80*$^{+}$	*1.39*$^{+}$	*1.54*$^{+}$	*1.81*$^{+}$	*2.35*$^{+}$	*4.20*$^{+}$	*6.46*$^{+}$	*9.53*$^{+}$
Butanone	0.28^{+}	0.31^{+}	0.32^{+}	0.47^{+}	0.83^{+}	1.25^{+}	1.72^{+}	2.35^{+}	3.16^{+}	3.79^{+}	4.75^{+}	7.43^{+}	12.7^{+}	17.9^{+}	27.6^{+}
	0.47^{+}	*0.38*$^{+}$	*0.43*$^{+}$	*0.62*$^{+}$	*0.90*$^{+}$	*1.47*$^{+}$	*1.72*$^{+}$	*2.28*$^{+}$	*3.50*$^{\pm}$	*4.01*$^{\pm}$	*5.54*$^{+}$	*7.73*$^{+}$	*13.5*$^{+}$	*20.0*$^{+}$	*33.6*$^{+}$
2-Pentanone	0.40^{+}	0.47^{+}	0.56^{+}	0.77^{+}	1.46^{+}	2.07^{+}	3.07^{+}	4.17^{+}	6.35^{+}	9.53^{+}	12.9^{+}	19.3^{+}	36.9^{+}	53.1^{+}	84.0^{+}
	0.70^{+}	*0.64*$^{+}$	*0.76*$^{+}$	*1.01*$^{+}$	*1.74*$^{+}$	*2.49*$^{+}$	*3.84*$^{+}$	*4.47*$^{\pm}$	*7.65*$^{\pm}$	*10.5*$^{-}$	*14.7*$^{\pm}$	*22.1*$^{+}$	*44.0*$^{+}$	*67.9*$^{+}$	*115*$^{+}$
2-Hexanone	0.57^{+}	0.64^{+}	0.83^{+}	1.24^{+}	2.29^{+}	3.38^{+}	5.01$^{\pm}$	7.20$^{\pm}$	12.5^{-}	19.2^{-}	30.9^{-}	52.3^{-}	-		
	0.97^{+}	*0.96*$^{+}$	*1.17*$^{+}$	*1.68*$^{+}$	*2.86*$^{+}$	*3.99*$^{\pm}$	*6.50*$^{\pm}$	*9.09*$^{\pm}$	*14.9*$^{-}$	*23.5*$^{-}$	*39.4*$^{-}$	*65.9*$^{-}$	-		
2-Heptanone	0.75^{+}	0.88^{+}	1.08^{+}	1.84^{+}	3.29^{+}	4.99^{+}	7.77$^{\pm}$	13.0^{-}	23.8^{-}	39.5^{-}	-	-	-		
	1.31^{+}	*1.39*$^{+}$	*1.73*$^{+}$	*2.63*$^{+}$	4.66’	*6.47*$^{\pm}$	11.4’	*16.3*$^{-}$	*30.4*$^{-}$	*53.0*$^{-}$	-	-	-		
2-Nonanone	1.17^{+}	1.48^{+}	1.93^{+}	3.44^{+}	6.55^{+}	10.6^{+}	20.0$^{\pm}$	31.3^{-}	-	-	-	-	-		
	2.31^{+}	*2.71*$^{+}$	*3.59*$^{+}$	*5.81*$^{+}$	*12.1*$^{\pm}$	*18.9*$^{-}$	*31.3*$^{-}$	*52.0*$^{-}$	-	-	-	-	-		
1-Alkylacetates															
Ethylacetate	0.34^{+}	0.35^{+}	0.50^{+}	0.71^{+}	1.22^{+}	1.88^{+}	2.60$^{\pm}$	3.53$^{\pm}$	5.23^{-}	7.02^{-}	9.89^{+}	13.5^{+}	23.9^{+}	33.6^{+}	53.7^{+}
	0.53^{+}	*0.52*$^{+}$	*0.59*$^{+}$	*0.84*$^{+}$	*1.40*$^{+}$	*2.01*$^{+}$	*2.65*$^{\pm}$	*3.75*$^{\pm}$	*6.00*$^{\pm}$	*7.92*$^{\pm}$	*10.9*$^{+}$	*14.6*$^{+}$	*27.3*$^{+}$	*42.7*$^{+}$	*69.4*$^{+}$
1-Propylacetate	0.51^{+}	0.61^{+}	0.77^{+}	1.07^{+}	1.99^{+}	3.04^{+}	4.48$^{\pm}$	6.22$^{\pm}$	11.6^{-}	15.5^{-}	23.7^{-}	37.7^{+}	75.4^{+}		
	0.86^{+}	*0.82*$^{+}$	*0.95*$^{+}$	*1.45*$^{+}$	*2.47*$^{+}$	*3.51*$^{+}$	*4.85*$^{\pm}$	*7.98*$^{\pm}$	*12.0*$^{\pm}$	17.8	*28.7*$^{-}$	44.7’	*100*$^{+}$		
1-Butylacetate	0.63^{+}	0.81^{+}	1.02^{+}	1.66^{+}	2.94^{+}	4.52^{+}	7.02$^{\pm}$	11.7^{-}	21.0^{-}	31.2^{-}	55.7^{-}	101^{-}	-		
	1.14^{+}	*1.21*$^{+}$	*1.49*$^{+}$	*2.24*$^{+}$	*3.98*$^{+}$	*5.66*$^{+}$	*9.59*$^{\pm}$	*14.0*$^{\pm}$	*24.6*$^{-}$	*40.7*$^{-}$	*79.7*$^{-}$	*142*$^{\pm}$	-		
1-Pentylacetate	0.87^{+}	1.07^{+}	1.32^{+}	2.25^{+}	4.18^{+}	6.64$^{\pm}$	11.5$^{\pm}$	18.3^{-}	36.9^{-}	62.3^{-}	-	-	-		
	1.47^{+}	*1.71*$^{+}$	*2.10*$^{+}$	*3.41*$^{+}$	*6.12*$^{+}$	*8.87*$^{\pm}$	*15.9*$^{\pm}$	*24.4*$^{-}$	*48.8*$^{-}$	*92.4*$^{-}$	-	-	-		
1-Heptylacetate	1.34^{+}	1.72^{+}	2.45^{+}	4.27^{+}	8.26^{+}	13.9$^{\pm}$	26.0$^{\pm}$	41.7^{-}	-	-	-	-	-		
	2.70^{+}	*3.31*$^{+}$	*4.23*$^{+}$	*8.60*$^{+}$	*15.9*$^{+}$	*25.7*$^{\pm}$	*43.9*$^{\pm}$	*78.4*$^{-}$	-	-	-	-	-		
1-Decylacetate	2.47^{+}	3.45^{+}	4.43^{+}	10.6^{+}	20.4’	37.0’	51.3^{-}	-	-	-	-	-	-		
	6.36^{+}	*10.3*$^{+}$	*12.2*$^{+}$	*27.3*$^{+}$	*56.5*$^{\pm}$	*101*$^{-}$	-	-	-	-	-	-	-		
n-Alkanes															
Pentane	1.07^{-}	2.41^{-}	3.48’	5.33’	10.0’	15.5’	26.5^{-}	47.4^{-}	-	-	-	-	-		
	4.42^{0}	*5.81*^{0}	6.93’	12.8”	226	37.00	-	-	-	-	-	-	-		
Hexane	2.17^{-}	2.77^{-}	3.90’	6.81^{-}	13.4^{-}	-	-	-	-	-	-	-	-		
	6.08^{0}	7.93’	*10.1*^{0}	*19.8*^{0}	35.90	-	-	-	-	-	-	-	-		
Heptane	2.76’	3.42^{-}	4.21’	8.89^{-}	18.5^{-}	-	-	-	-	-	-	-	-		
	8.20”	11.0“	13.9“	*28.3*^{0}	*55.6*^{0}	-	-	-	-	-	-	-	-		
Octane	3.47^{-}	4.17^{-}	5.22’	11.7^{-}	26.2^{-}	-	-	-	-	-	-	-	-		
	11.0^{0}	15.10	19.70	*41.7*^{0}	*88.1*^{0}	-	-	-	-	-	-	-	-		
Nonane	4.30“	4.87^{0}	6.69^{0}	15.1“	33.0^{-}	-	-	-	-	-	-	-	-		
	14.6^{0}	20.4’	*27.4*^{0}	*63.5*^{0}	*137*^{0}	-	-	-	-	-	-	-	-		
Dodecane	6.56^{0}	9.04^{0}	-	-	-	-	-	-	-	-	-	-	-		
	32.5^{0}	*51.0*^{0}	-	-	-	-	-	-	-	-	-	-	-		

TABLE II *(continued)*

Solute	φ_W														
	0.028	0.057	0.095	0.193	0.293	0.373	0.445	0.518	0.602	0.685	0.757	0.829	0.908	0.946	0.913
2,2-Dimethylalkanes															
2,2-Dimethyl-	**1.94**$^-$	2.77’	**3.38**$^-$	**6.16**$^-$	**11.6**$^-$	18.8’	-	-	-	-	-	-	-	-	-
butane	4.86	***6.50***^{0}	7.97“	***15.4***^{0}	279’	***45.5***^{0}	-	-	-	-	-	-	-	-	-
2,2-Dimethyl	**2.47**$^-$	3.59’	**4.45**$^-$	**8.12**$^-$	**15.6**$^-$	**26.8**$^-$	-	-	-	-	-	-	-	-	-
pentane	6.64’	9.09”	***11.3***^{0}	***19.7***^{0}	43.8”	72.9’	-	-	-	-	-	-	-	-	-
2,2-Dimethyl-	3.18’	3.82’	**4.92**$^-$	**10.8**$^-$	21.6”	-	-	-	-	-	-	-	-	-	-
hexane	***8.64***^{0}	***12.3***^{0}	***15.5***^{0}	31.8”	***65.2***^{0}	-	-	-	-	-	-	-	-	-	-

The standard deviation of the areal retention volumes was calculated to be $\sigma_{V_{S,su/vNA}} = \pm(0.08 + 0.012 V_{S,su/vNA})$ μl/m². The sign of the associated system peak is given as a superscript ($^+$ and $^-$ for a system peak rich and poor in AN, respectively).

RESULTS AND DISCUSSION

As indicated in the Introduction, adsorption isotherms from AN-W mixtures are almost congruent on the two chemically modified (DMB and C_{14}) surfaces. Hence, the "hard" DMB surface can be considered as a reference, and a difference in areal retention volume on the C_{14} surface at the same eluent composition can unequivocally be attributed to the presence of the bonded alkyl chains. In the following, first the dependence of areal retention on composition on the DMB surface will be discussed, then the additional retention on the C_{14} surface. The system peak accompanying the injection of a pure solute can be positive or negative, i.e., rich or poor in AN. An interpretation of the sign of this system peak will also be given.

Solute retention as a function of eluent composition

The dependence of the areal retention volume, $V_{S,su/vNA}$, on eluent composition shows the often reported general trend of increasing retention with increasing water content and also with increasing carbon number of the homologues. In Fig. 4 are plotted, as an illustration, areal retention volumes on the DMB surface, $V^{DMB}_{S,su/vNA}$, for homologous 1-alkanols as a function of the volume fraction of water in the eluent, φ_W. This example is particularly interesting because several homologues could be measured in the whole or in a broad concentration range. This general trend is the same for other homologous series and is also observed for data on the C_{14} surface. The plot suggests that the composition dependence of the retention of all solutes follows a similar law when choosing an individual starting point for each solute on the composition scale.

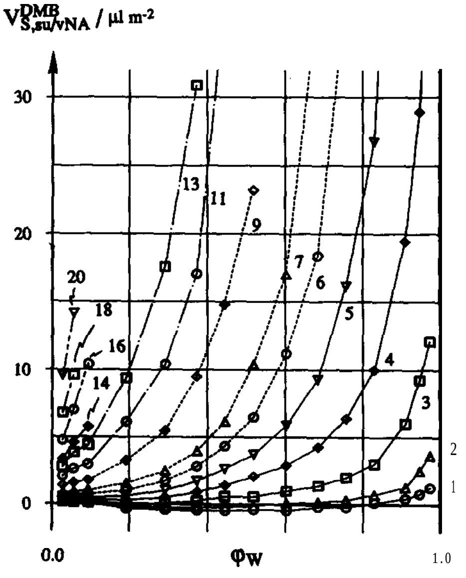

Fig. 4. Areal retention volumes, $V^{DMB}_{S,su/vNA}$, of 1-alkanols, $C_zH_{2z+1}OH$ with z = 1-20 as indicated, on the DMB-covered surface as a function of the volume fraction of water, φ_W, in the binary AN-W eluent.

Two equations are widely used to describe retention as a function of eluent composition. The most often used, due to Snyder [42] and Soczewinski [43], proposes that the logarithm of retention is a linear function of the logarithm of the volume fraction of the organic component. The second equation, due to Schoenmakers *et al.* [44], proposes a quadratic expression for the dependence of the logarithm of retention on the eluent composition. Neither equation is applicable to areal retention volumes in the vNA convention, $V_{S,su/vNA}$, because this retention characteristic can be negative (e.g., methanol and ethanol; see Fig. 4).

Areal retention volumes determined with reference to the vNA convention, $V_{S,su/vNA}$, differ from those referring to a hold-up volume with a stationary layer of τ = 15 A, $V_{S,su/15}$, by a constant of 1.5 μl/m^2, as explained under Theoretical Background (see eqn. 15). This areal retention is never negative because it corresponds to the minimum layer thickness determined by the minimum slope of the excess adsorption isotherm of the eluent components [7]. Further, the areal τ retention volume with τ = 15 Å, $V_{S,su/15}$, is roughly proportional to capacity factors reported in the literature where the hold-up volume has been determined with a solute which at all compositions has been believed to be less adsorbed than either component of the eluent. Consequently, this areal retention volume and/or the related distribution coefficient, $K_{D,su/15}$, is suitable for examining the validity of the Snyder–Soczewinski and the Schoenmakers equations:

$$\ln K_{D,su/15} = A + B\ln\varphi_{AN} \tag{19}$$

$$\ln K_{D,su/15} = a + b\varphi_W + c(\varphi_W)^2 \tag{20}$$

Eqns. 19 and 20 were originally formulated for the logarithm of the capacity factor. The distribution coefficient, $K_{D,su/15}$, is proportional to the areal retention volume, hence it is also roughly proportional to literature capacity factors. Consequently, the original equations differ from eqns. 19 and 20 by a common constant for all solutes.

At first sight, it is obvious that neither equation can describe retention in the whole composition range. Fig. 5 shows the plot of the logarithm of the

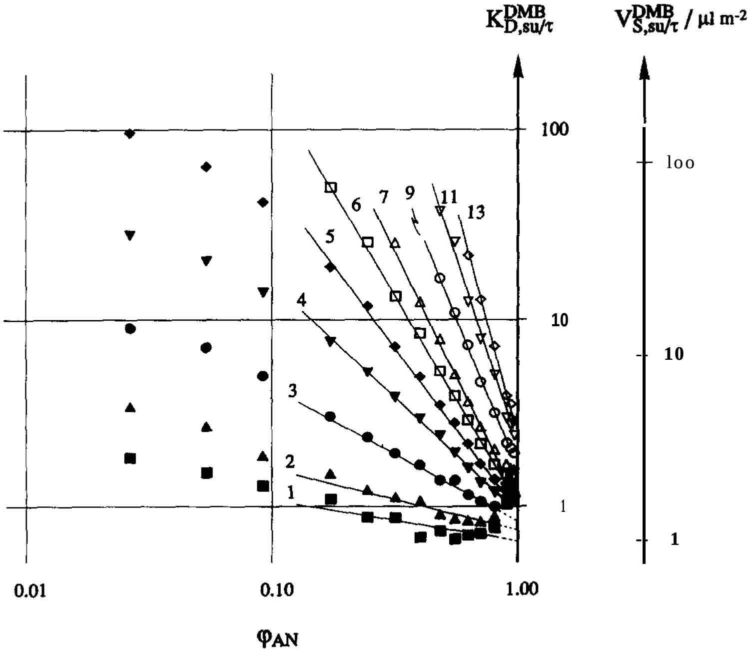

Fig. 5. Illustration of the use ofeqn. 19 for the description of the composition dependence of the logarithm of the distribution coefficient, $\ln K^{DMB}_{D,su/\tau}$, with a stationary phase thickness of τ = 15 Å on the example of I-alkanols, $C_zH_{2z+1}OH$ with z = 1–13 as indicated, on the DMB-covered surface. Solid lines are traces of the linear regression of $\ln K^{DMB}_{D,su/\tau}$ fitted to experimental points in the composition range φ_{AN} = 0.1–0.9. The scale of the areal τ retention volumes is also shown.

distribution coefficient on the DMB surface, $\ln K^{DMB}_{D,su/15}$, of the 1-alkanols as a function of the logarithm of the volume fraction of acetonitrile in the eluent, $\ln\varphi_{AN}$. For comparison, the logarithmic areal τ retention volume scale, $\ln V^{DMB}_{S,su/15}$, is also shown in Fig. 5. It is seen that the plot is fairly linear in the composition range $0.1 < \varphi_{AN} < 0.9$, with the exception of weakly retained homologues. The Snyder-Soczewinski plot for other solutes confirms these qualitative conclusions. Based on the underlying model the slope, *B*, of eqn. 19 should be proportional to the molar volume of the solutes. Fig. 6 shows the plot of the constant *B* of all solutes on the DMB surface as a function of the molar volume. The plot is strongly curved for weakly retained solutes, and further, the constant *B* seems to depend also on the polarity of the solutes.

The applicability of eqn. 20 is illustrated in Fig. 7, where solid lines represent quadratic regressions in the composition range $0.0 < \varphi_W < 0.9$, where the representation of experimental points by eqn. 20 is very satisfactory as was pointed out by Schoenmakers *et al.* [45]. The dotted lines show the quadratic regressions if all points are included in the

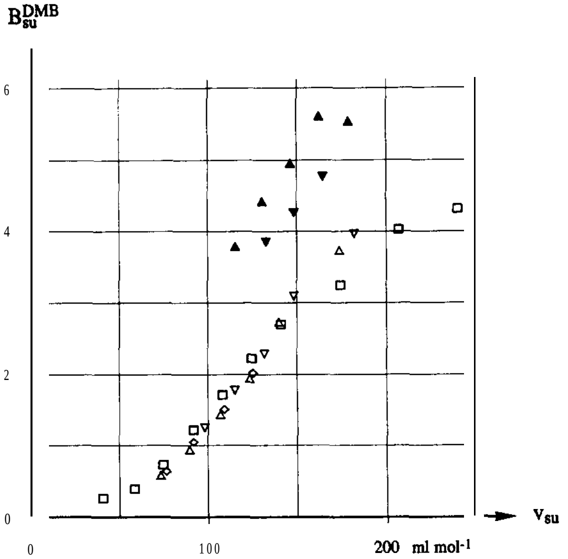

Fig. 6. Value of the constant B^{DMB}_{su} (slope) in the linear regression eqn. 19 (the logarithm of the distribution coefficient, $\ln K^{DMB}_{D,su/\tau}$, with τ = 15 Å vs. the logarithm of the volume fraction of AN in the eluent, $\ln\varphi_{AN}$) as a function of the molar volume of the solutes, v_{su}. Experimental points outside the composition range φ_{AN} = 0.1–0.9 were not considered for the regression (see text and Fig. 5). ▲ = n-Alkanes; ▼ = 2,2-dimethylalkanes; □ = 1-alkanols; 0 = 2-alkanols; △ = 2-alkanones; ▽ = 1-alkyl acetates.

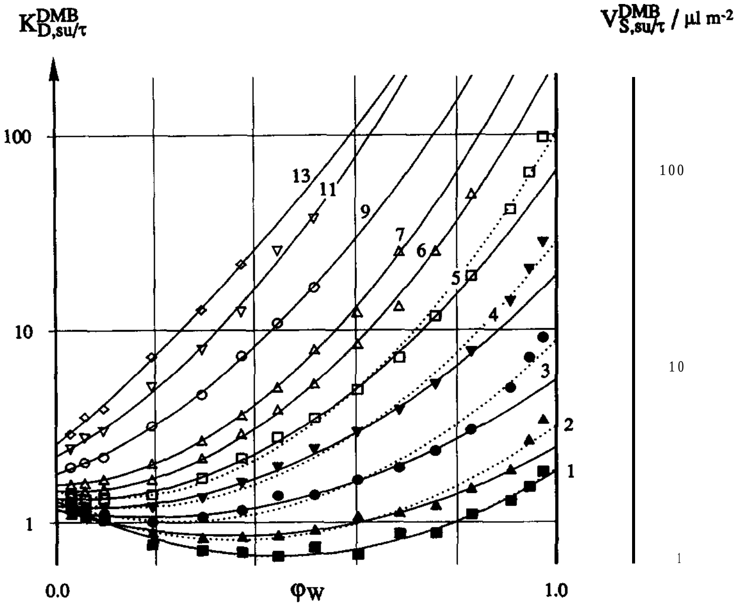

Fig. 7. Illustration of the description of the composition dependence of the logarithm of the distribution coefficients, $\ln K^{DMB}_{D,su/\tau}$, calculated with τ = 15 A, by eqn. 20 as a function of the volume fraction of water, φ_W, in the binary AN-W eluent on the example of I-alkanols, $C_zH_{2z+1}OH$ with z = 1-13 as indicated, on the DMB-covered surface. Solid lines are traces of the quadratic eqn. 20 fitted to points in the range φ_W = 0.0–0.9; dotted lines are traces of eqn. 20 fitted to all experimental points including those in the water-rich region. The scale of the areal τ retention volumes is also shown.

whole composition domain. It is interesting that this regression is suitable for extrapolation to pure acetonitrile as eluent but gives erroneous results for pure water. Based on the underlying model [44], the value of the volume fraction of water at the minimum retention, $\varphi_{W,min}$, either real or hypothetical, calculated from the quadratic regression for moderately retained solutes, should be related to the Hildebrand solubility parameter of the eluent components, δ_{AN} and δ_W, and that of the solute, δ_{su}, according to

$$\varphi_{W,min} = -b/2c = (\delta_{su} - \delta_{AN})/(\delta_W - \delta_{AN}) \qquad (21)$$

In Fig. 8 the experimental value of the volume fraction of water at minimum retention, $\varphi_{W,min}$(exp), is plotted as a function of the value predicted by eqn. 21 for weakly retained solutes. The correlation is poor.

In summary, the two-parameter eqn. 19 describes solute retention as a function of eluent composition in the domain φ_W = 0.1–0.9, whereas the three-parameter eqn. 20 is applicable in the range φ_W = 0.0–0.9. With these restrictions in mind, both equations are well suited for interpolation but are poorly related to their respective underlying models.

Additional retention on the C_{14} surface

Areal retention volumes as a function of eluent composition show similar trends on the C_{14} and DMB surfaces. For a first comparison, regression coefficient of the Snyder-Soczewinski equation were calculated in the range φ_W = 0.1–0.9 on both adsorbents by using distribution coefficients, $K_{D,su/15}$. In Fig. 9 is shown the plot of the intercept, *A*, of eqn. 19 on the C_{14} surface as a function of the intercept, *A*, obtained on the reference surface, DMB. Fig. 10 shows the analogous plot of the constant *B* in eqn. 19, showing that the value of the constant is about the same on both surfaces. The value of the intercept *A* is also the same on both surfaces for weakly retained solutes, whereas for more strongly adsorbed solutes the intercept A on the C_{14} surface is about twice that on the DMB reference. Intercept *A* is interpreted as the logarithm of the distribution coefficient in a hypothetical pure acetonitrile (recall that eqn. 19 is only valid up to φ_{AN} = 0.9). In summary, the distribution coefficient at φ_{AN} = 1 of weakly retained solutes is the same on both surfaces, whereas for strongly retained solutes they are related by

$$K_{D,su/15}^{C_{14}} = (K_{D,su/15}^{DMB})^2 \qquad (\varphi_{AN} = 1) \qquad (22)$$

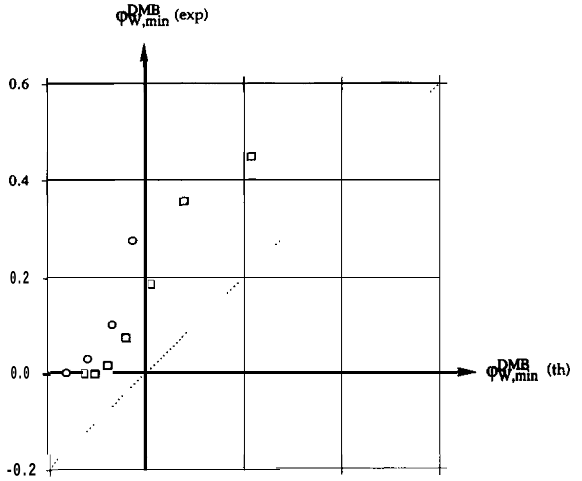

Fig. 8. Composition of the binary AN-W mixture at which retention is minimum on the DMB-covered surface, $\varphi_{W,min}^{DMB}$, as a function of its theoretical value. Experimental minima are calculated from eqn. 20 fitted to experimental points in the range φ_W = 0.0–0.9; theoretical composition of the binary eluent at minimum retention is calculated with eqn. 21. □ = I-Alkanols; 0 = 2-alkanols; 0 = 2-alkanones.

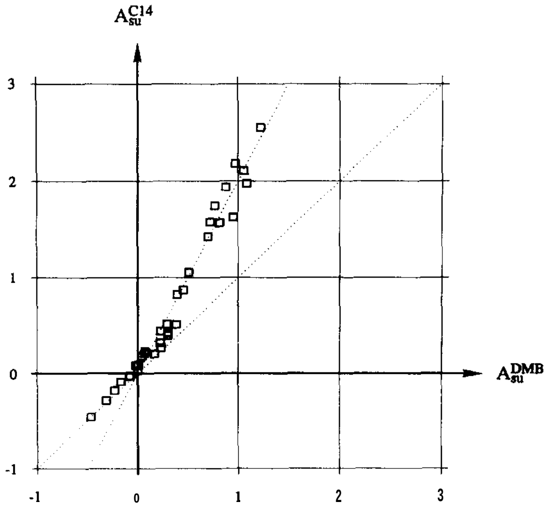

Fig. 9. Plot of coefficients *A* of the Snyder-Soczewinski equation (eqn. 19) fitted to experimental points determined on the C_{14} graft as a function of those found on the DMB reference surface.

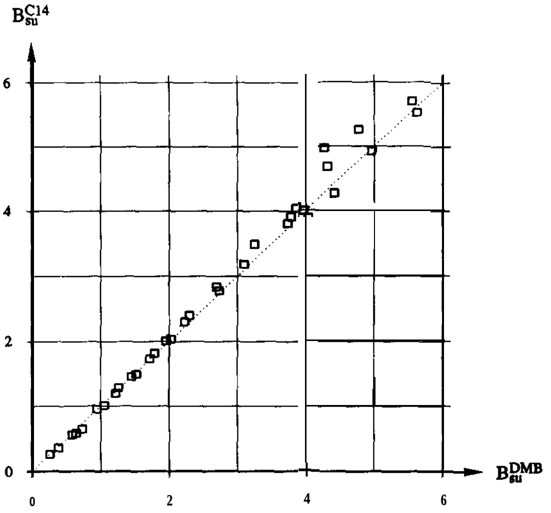

Fig. 10. Plot of the slope *B* of the Snyder-Soczewinski equation (eqn. 19) fitted to experimental points determined on the C_{14} graft as a function of those found on the DMB reference surface.

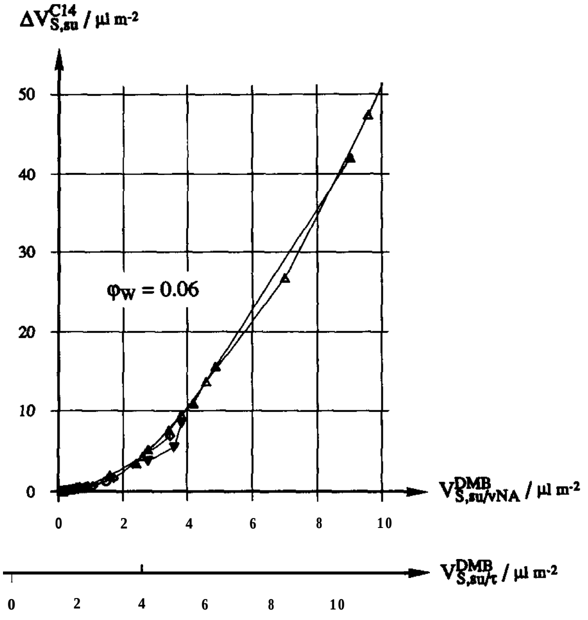

Fig. 11. Additional areal retention volumes on the C_{14}-covered surface, $\Delta V^{C_{14}}_{S,su}$, plotted as a function of areal retention volumes measured on the DMB reference surface, $V^{DMB}_{S,su//vNA}$, at the composition φ_W = 6% of the AN-W binary eluent. The scale of the areal τ retention volumes, with $\tau = 15$ A, is also shown. A = n-Alkanes; ▼ = 2,2-dimethylalkanes; △ = 1-alkanols; ▽ = 2-alkanols; 0 = 2-alkanones; 0 = I-alkyl acetates.

The change in correlation laws suggests different retention mechanisms for weakly and strongly retained (adsorbed) solutes.

In order to examine differences in retention in the whole composition range, let us examine the behaviour of the function $\Delta V^{C_{14}}_{S,su}$ defined as

$$\Delta V^{C_{14}}_{S,su} = V^{C_{14}}_{S,su/vNA} - V^{DMB}_{S,su/vNA} \cong V^{C_{14}}_{S,su/\tau} - V^{DMB}_{S,su/\tau}$$

$$(\varphi_W = \text{constant}) \qquad (23)$$

i.e., the additional areal retention volume on the C_{14} surface at the same eluent composition. This additional retention is independent of the hold-up volume definition. As examples, in Figs. 11 and 12 additional retention volumes are plotted as a function of the areal retention volumes on the reference surface, $V^{DMB}_{S,su/vNA}$, at two different eluent compositions. The latter retention measures the adsorption strength of the solute on a "hard" non-polar surface. It is seen that the additional retention is independent of the nature of the solute. As a main effect, the additional retention is proportional to retention on the reference surface, DMB, where its dependence

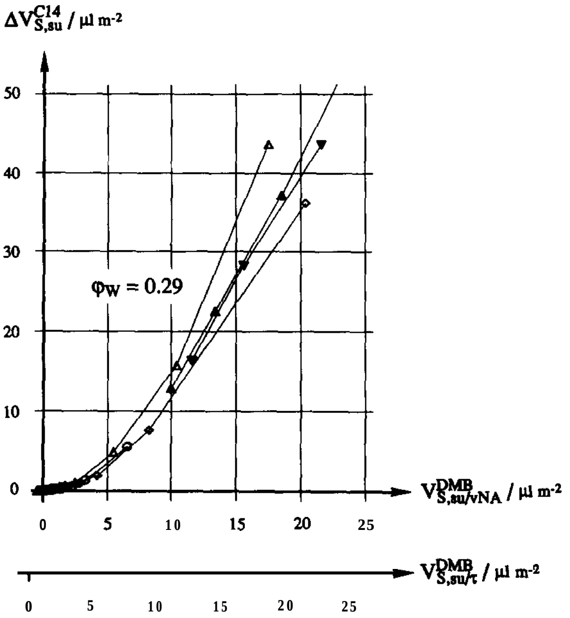

Fig. 12. Additional areal retention volumes on the C_{14}-covered surface, $A\ V^{C_{14}}_{S,su}$, plotted as a function of areal retention volumes measured on the DMB reference surface, $V^{DMB}_{S,su/vNA}$, at the composition φ_W = 29% of the AN-W binary eluent. The scale of the areal 7 retention volumes, with τ = 15 A, is also shown. Symbols as in Fig. 11.

can be approximated by the following one-parameter equation:

$$\Delta V_{S,su}^{C_{14}} = C(\varphi_W)(V_{S,su/vNA}^{DMB})^2 \quad (24)$$

In Fig. 13 the coefficient $C(\varphi_W)$ is plotted as a function of the composition of the eluent, φ_W. It is seen that the dependence of the additional retention on adsorption strength decreases with increasing water content in the eluent. In Fig. 14 the additional retention is plotted as a function of composition, φ_W, and areal retention volume on the reference surface, $V_{S,su/vNA}^{DMB}$, as a three-dimensional graph. As a general rule the retention increasing effect of the C_{14} graft is zero for slightly retained solutes and is less and less pronounced with increasing water concentration in the AN-W mixture.

The sign of the system peak

The slight perturbation of the composition of an m-component eluent gives rise to a set of $m - 1$ system peaks (also called concentration peaks [6] or eigenpeaks [46]). Injection of a small amount of an n-component solute mixture also perturbs the composition and will result in $m + n - 1$ peaks, of which n are called solute peaks and the remaining $m-1$ are the associated system peaks. A solute peak will comprise one of the solutes contained in the solute mixture together with the m components of the eluent but, as a general rule, the concentration ratio of the eluent components will be different from that of the eluent mixture. The $m - 1$ associated system peaks, each having a different composition, contain only the n components of the eluent. The mathematical treatment of such a general case leads to the DeVault matrix [47]. An eigenvalue of the matrix corresponds to the retention characteristics of a peak [6,35,46,48] whereas the associated eigenvector is the composition in the column section where the peak is located [47,49,50]. Although the mathematical solution is known, "... it remains difficult to develop an intuitive direct understanding of the phenomena", as pointed out by Poppe [SO]. Nevertheless, several attempts have been made to relate concentration changes under the peak to solvent displacement by the solute at the liquid-adsorbent interface [51,52] or to its preferential solvation in the eluent [53] or to a combination of both [46].

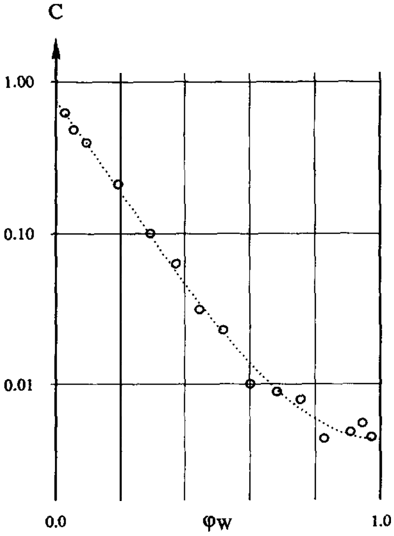

Fig. 13. Plot of coefficient Cin eqn. 24 (logarithmic scale) relating additional retention on the C_{14} surface to the square of areal retention on the DMB surface as a function of the volume fraction of water in the binary AN-W eluent. The dotted line is the trace of the cubic polynomial regression of the logarithm of C on the volume fraction of water.

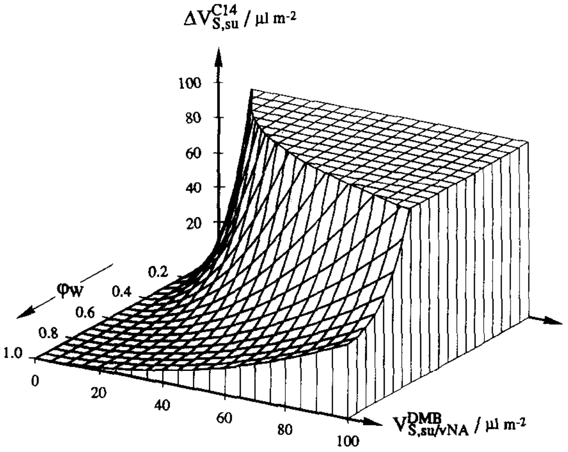

Fig. 14. Additional retention volume on the C_{14} surface, $\Delta V_{S,su}^{C_{14}}$, as a function of the areal retention volume ofsolutes on the DMB reference surface, $V_{S,su/vNA}^{DMB}$, and of the volume fraction of water in the binary AN-W eluent, φ_W. The surface is calculated with eqn. 24 using coefficients $C(\varphi_W)$ obtained by the regression shown in Fig. 13.

In a binary eluent mixture the phenomenon is greatly simplified as there will be only one system peak with invariant retention. Its retention volume is proportional to the slope of the excess adsorption isotherm of the binary eluent (see eqn. 6). In the binary organic solvent-water mixture, a slight perturbation may be induced either by injection of the organic component or by injection of water, both provoking a system peak of the same retention and magnitude but of the opposite sign. In the following we shall designate a system peak as positive if it originates from injection of the organic component, and consequently the composition under the peak is richer in the organic component compared with the eluent, and as a negative system peak in the opposite case. As a general rule, the system peak also appears when a pure solute or a mixture of solutes is injected. As already noted by Melander et *al.* [46], the amplitude of the system peak which accompanies the peak of a pure solute, its "associated system peak", gives valuable additional information on the adsorption mechanism of the solute in question.

Let us put forward the question of the sign and amplitude of the associated system peak. In Fig. 15 is illustrated the origin of the system peak for two extreme situations. In the first case, for a non-retained solute, there will be a concentration change in the binary eluent by preferential solvation. The corresponding excess solvation isotherm (see Fig. 15a) can be deduced by analogy with excess isotherms observed on adsorbents. A non-polar solute (N in Fig. 15) will have a (+)U-type solvation isotherm, where the sign (+) designates an organic-rich solvate layer. An amphiphilic molecule (A in Fig. 15) should have, as a general rule, a (−/+)S-type isotherm, *i.e.,* it will be preferentially solvated by water at low water concentrations (strong interaction of water with the hydrophilic head) and by the organic component at high water contents. Finally, solvation of a polar-type molecule (P in Fig. 15) must have a (-)U-type excess isotherm. In the column section where the solute is dissolved there will be a perturbation of the eluent composition of the opposite sign. Consequently, non- or weakly retained non-polar solutes will provoke a negative system peak, a non-retained polar solute will give rise to a positive system peak and the sign of the system peak associated with a non-retained amphiphilic molecule will change the sign from positive to negative with increasing water concentration. It is obvious that the sign of the system peak of a non-retained solute is independent of the nature of the adsorbent.

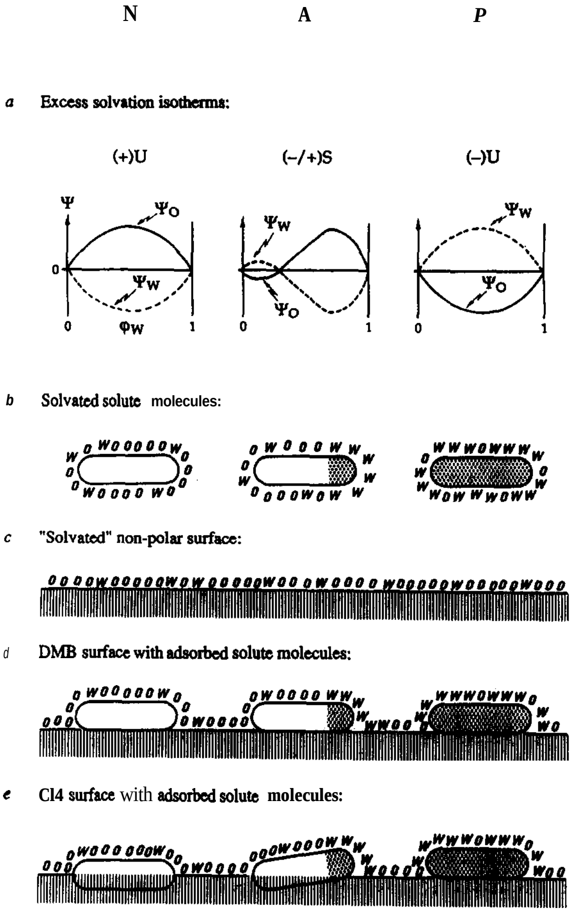

Fig. 15. Illustration of preferential (excess) adsorption on the surface of a non-polar adsorbent and of the preferential solvation of N = non-polar, A =amphiphilic and P = polar solutes in contact with an organic liquid-water (O-W) binary mixture. (a) Solvation excess isotherms of solutes of different polarity as a function of the water content in the O-W mixture: (+)U-type isotherm of non-polar solutes (N), (-/+)S-type isotherm of amphiphilic solutes (A) and (-)U-type isotherm due to preferential solvation by water of polar solutes (P). (b, c) Solvation/adsorption layers from the O-W mixture at some intermediate composition; (b) preferential solvation of solutes and (c) organic-rich adsorption layer near the non-polar surface in the absence of solutes. (d, e) Change of the adsorption layer in the presence of different types of adsorbed solutes on the hard DMB and the penetrable C_{14} graft, respectively.

For the second extreme case of a strongly retained solute, the effect of preferential solvation can be neglected. In fact, such a molecule will most of the time be adsorbed and constitute part of the surface of the adsorbent. In Fig. 15c is illustrated the preferential adsorption of the organic component of the eluent on a non-polar surface, such as DMB and C_{14}, following a (+)U-type excess isotherm. This isotherm will be only slightly perturbed by an adsorbed non-polar molecule on a hard-type non-polar DMB surface (see Fig. 15d) and even less on a soft-type (C_{14}) surface where the molecule can even penetrate the surface layer (see Fig. 15e). Consequently, there will be no or negligible perturbation of the isotherm and no or negligible system peak. Adsorption of polar-type and amphiphilic molecules will provoke throughout the whole composition range a positive system peak as the surface will become more hydrophilic with the adsorbed molecule.

This qualitative discussion concerning the sign of the associated system peak can be summarized as follows:

solute:	non-polar		amphiphilic		polar	
φ_W:	low	high	low	high	low	high
retention:						
weak:			+	−	+	
strong:	0		+	+	(+)	

Based on similar arguments, Melander et al. [46] arrived at essentially the same conclusions. Let us emphasize that all solutes have stronger retention at higher water concentrations, φ_W. Consequently, at low water content the sign of the system peak should be discussed following the rules of a weakly retained solute, whereas at high water contents the rules of strongly retained solutes should be considered. The observed sign of the associated system peak, listed in Table II, is in accordance with this qualitative discussion with the exception of methanol and ethanol. In fact, the solvation isotherm was discussed by assuming that the molecule in solution is an adsorbing "colloidal" particle having a surface on which the small molecules of the eluent are adsorbed. Solvation of small molecules such as methanol and ethanol, comparable in size to the eluent components, probably follows a different rule. In Table II the superscript $^{\pm}$ is used to indicate composition where the sign of the system peak was not significant due to change of sign. This behaviour was observed for some of the 2-alkanones and 1-alkyl acetates as amphiphilic solutes on both surfaces at decreasing water concentrations for higher homologues. The change of sign takes place at about the same value of retention for a homologous series and corresponds to a compensation of solvation and adsorption effects. On the DMB surface, alkanes as non-polar solutes show a negative system peak which becomes zero at higher retentions where the fraction of solute molecules further away from the surface is negligible. The absence of the system peak in such cases is indicated in Table II with the superscript zero. No system peak was observed for alkanes and isoalkanes on the C_{14} surface where non-polar solutes might penetrate into the liquid-like bulk of the C_{14} chains.

CONCLUSIONS

It has been shown that retention of a solute on a non-polar adsorbent having grafted C_{14} chains can be given as a function of its retention on the hard non-polar standard DMB surface. Combination of eqns. 23 and 24 gives

$$V^{\mathrm{Alkyl}}_{\mathrm{S,su/vNA}} = V^{\mathrm{DMB}}_{\mathrm{S,su/vNA}}(1 + C^{\mathrm{Alkyl}} V^{\mathrm{DMB}}_{\mathrm{S,su/vNA}}) \qquad (25)$$

The dependence of the areal retention volume on the DMB surface, $V^{\mathrm{DMB}}_{\mathrm{S,su/vNA}}$, as a function of the eluent composition can be described by eqns. 19 and 20 in their respective validity domains. Also, the coefficient C^{Alkyl} in eqn. 25 is a function of the composition but, to a first approximation, independent of the nature (polarity) of the solute, hence the function $C^{\mathrm{Alkyl}}(\varphi_W)$ seems to be a characteristic of the (non-polar) stationary phase in question and of the organic component in the O-W binary eluent. On the C_{14} surface, it decreases from its highest value in pure acetonitrile to very low values in the water-rich region following an exponential law as a function of the volume fraction of water, φ_W. Its amplitude being a measure of the additional retention on the surface with alkyl grafts, we conclude that the latter surface becomes increasingly similar to the hard DMB adsorbent with increasing water content.

In eqn. 25, the symbol of the areal retention on the surface with alkyl graft is designated by the superscript Alkyl instead of C_{14}, indicating that we believe that this equation is of general validity for non-polar adsorbents with grafted chains. The validity of this generalization remains to be proved, but its possibility is strongly suggested by findings on such stationary phases reported in the literature (see Introduction). In fact, the similar behaviour of such stationary phases has been repeatedly demonstrated and it is generally admitted that additional retention is positive and increases with increasing chain length and increasing density of the graft. Obviously, differences between such adsorbents will be accounted for by the function $C^{\mathrm{Alkyl}}(\varphi_{\mathrm{W}})$.

The excess adsorption isotherms at the interface between the AN-W mixtures and the DMB and C_{14} adsorbents are nearly congruent, as shown in Fig. 1. This result implies that acetonitrile does not penetrate the C_{14} surface, *i.e.*, both surfaces are very similar in contact with this eluent. On the other hand, the additional retention of the solutes on the C_{14} graft can only be explained if possible penetration of the solutes into the C_{14} surface is admitted. With respect to solute behaviour, the similarity of the surfaces is given by the amplitude of the function $C^{\mathrm{Alkyl}}(\varphi_{\mathrm{W}})$, and consequently the adsorbents resemble each other most in contact with a water-rich eluent. Indeed, it seems to be logical that the C_{14} graft is "softer" in contact with the organic component and becomes harder and harder in contact with water-rich eluents, where the C_{14} chains are increasingly strongly excluded from the liquid by a similar law that is valid for non-polar solutes such as alkanes. Solid-state ^{2}H-NMR studies by Zeigler and Maciel [54] of silicas covered by deuterated C_{18} chains in contact with liquids of different polarity seem to confirm these conclusions.

ACKNOWLEDGEMENTS

This paper reports on part of a project financed by the "Fonds National Suisse de la Recherche Scientifique". Technical help from Y. Bessard and Ph. Jacquemet is greatfully acknowledged. Deuterated solvents were a gift from Chemie Uetikon (Switzerland). Thanks are due to François Riedo of the "École d'Ingénieurs de Fribourg", Switzerland, for discussions and to Professor H. Poppe for his criticism and suggestions.

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